



Influence of H₂S on ZrO₂-based gasification gas clean-up catalysts: MeOH temperature-programmed reaction study

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ABSTRACT

Addition of H₂S in the gasification gas stream has been found to improve naphthalene and ammonia conversion over ZrO₂ and Y₂O₃-ZrO₂ catalysts, whereas over SiO₂-ZrO₂ such effect has not been observed. The differences in the properties of the catalysts were studied by spectroscopic (MeOH-DRIFTS) and temperature-programmed methods (H₂S-TPD and MeOH-TPSR). Methanol was also used to probe the changes after sulfidation of the catalysts. H₂S adsorption sites were found to be different on the ZrO₂ and Y₂O₃-ZrO₂ catalysts compared with the ones on the SiO₂-ZrO₂ catalyst. Sulfur was also found to be more reactive on the ZrO₂ and Y₂O₃-ZrO₂ catalysts than on SiO₂-ZrO₂. It was suggested, that the positive effect of H₂S on naphthalene conversion during gasification gas clean-up is connected with the reactions of adsorbed sulfur on their surface. In contrast, on SiO₂-ZrO₂ the lack of such an effect may be related to limited reactivity of sulfur on the surface.

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1. Introduction

Gasification is the first processing step required in synthesis gas production from biomass, which provides a prominent alternative route to environmentally friendly liquid fuels. The produced H₂-rich gas from e.g. wood residues, straw or peat has to be cleaned from impurities such as tar and ammonia to avoid plugging in the downstream equipment [1,2]. Zirconia-based catalysts are known to be active in gasification gas clean-up processes in the presence of oxygen [3]. Since the biomass gasification gas contains considerable amounts of H₂S, even up to 500 ppm, sulfur tolerance of the catalyst is crucial [4]. The effect of H₂S on the gasification gas clean-up activities of ZrO₂, Y₂O₃-ZrO₂, and SiO₂-ZrO₂ catalysts at 600–900 °C was investigated by Rönkkönen et al. [4]. At 600 and 700 °C addition of H₂S enhanced the activity of Y₂O₃-ZrO₂ and ZrO₂, whereas mainly sulfur poisoning was observed for SiO₂-ZrO₂. The intensity of the enhancement effect was related to the catalyst's Lewis basicity, and the amount of reactive oxygen on the catalyst. It was suggested that sulfur adsorption contributes to the generation of a new type of active sites, possibly also affecting the surface properties of the catalysts [4].

Generally, sulfur has been found to affect the behavior of catalysts in several applications. Addition of H₂S enhances the activity of ZrO₂ in isopropanol decomposition, since when H₂S is adsorbed on the ZrO₂ surface, oxygen is replaced by sulfur ions causing an increase in the basicity and/or redox properties of ZrO₂ [5]. In an IR spectroscopic study performed by Travert et al. [6], adsorption of H₂S was shown to induce strong modifications in the surface acidic properties of SiO₂, Al₂O₃, TiO₂ and ZrO₂. The concentration of Lewis acid sites, i.e. coordinatively unsaturated (c.u.s.) metal cationic Mⁿ⁺ sites, on these catalysts was found to decrease by titration with adsorbed sulfur species. Simultaneously, an increase in the number of Brønsted acid sites was observed by the formation of OH⁻ groups as a result of dissociative adsorption of H₂S [6].

The Lewis basicity of ZrO₂ is claimed to originate from its c.u.s. O²⁻ centers [7], whereas the Zr⁴⁺ sites are known to be centers for Lewis acidity [8]. Thus, the dry surface of ZrO₂ has Zr⁴⁺-O²⁻ Lewis acid-base pairs, which may be saturated by dissociated water species forming hydroxyl groups. The hydroxyl groups are amphoteric in nature, thus acting as a source for either Brønsted acidity or basicity [8]. In the gasification gas clean-up, the catalyst performance is largely affected by the mobility of lattice oxygen and the formation of oxygen vacancies, since the lattice oxygen is believed to take part in the tar (toluene, naphthalene, etc.) oxidation reactions [2,4,9]. In general, (intrinsic) oxygen vacancies are formed on ZrO₂ via reduction of the surface. Extrinsic oxygen vacancies are induced by other metals in the lattice, which enhance the

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performance of e.g. $\text{Y}_2\text{O}_3\text{-ZrO}_2$ compared to ZrO_2 [10]. It has been observed for the partial oxidation of methane that the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ system possesses superior properties compared to ZrO_2 due to the increased lattice oxygen diffusion and fast oxygen exchange of the doped oxide [11]. On the contrary, SiO_2 is not expected to create oxygen vacancies on ZrO_2 [12].

Studies on the influence of H_2S suggest that the modification of the catalyst properties are caused by changes in the acidic, basic, or redox properties of the catalyst. These properties can be studied by the methanol probe reaction. Vibrational spectroscopic techniques characterize the catalyst surface based on the adsorbed methoxy type species derived from methanol [13]. On the other hand, the gaseous desorption products generally indicate the chemical nature of the surface sites; formaldehyde (CH_2O) indicates the presence of redox sites, dimethyl ether (CH_3OCH_3 , DME) acidic sites, and carbon oxides basic sites. Several publications exist on MeOH adsorption and its surface reaction on metal oxides surfaces [14–19]. Less is known about MeOH adsorption on the sulfided metal oxide surfaces.

The aim of this study was to elucidate the observed H_2S -induced changes in the properties of the zirconia-based catalysts, especially regarding the sulfided catalysts' different behavior in naphthalene conversion during gasification gas clean-up (improvement for ZrO_2 and $\text{Y}_2\text{O}_3\text{-ZrO}_2$ compared to no effect for $\text{SiO}_2\text{-ZrO}_2$). First, methanol was used as a surface probe molecule to characterize the untreated catalysts. The catalysts were also probed with H_2S . Finally, MeOH adsorption was performed on the sulfided catalysts to study the effect of H_2S on the catalyst properties.

2. Experimental

ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$ with 5 mol-% Y_2O_3 , and $\text{SiO}_2\text{-ZrO}_2$ with 8 mol-% SiO_2 from MEL Chemicals were used as catalysts. The catalysts were calcined at 800 °C for 1 h. These catalysts have been previously characterized by Viinikainen et al. [2]. The surface characterization indicated that the surface sites of these catalysts varied. Raman and XRD characterizations showed that ZrO_2 was monoclinic, but $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ were mixtures of tetragonal and cubic structures. The specific surface area was found to differ (for ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$ the surface areas were 24, 53, 92 m²/g, respectively) [2].

2.1. H_2S retention on the catalyst surface

H_2S temperature-programmed desorption (TPD) experiments were carried out in an Altamira AMI-100 characterization system to study the sulfur retention and probe the adsorption modes of H_2S on the studied catalyst. Prior to each experiment the samples were dried in N_2 (30 cm³/min) for 2 h at 150 °C. A gas mixture containing 15 cm³/min N_2 (AGA, 99.999%) and 15 cm³/min H_2S in H_2 (AGA, 0.1% H_2S in H_2) was passed through powder form catalyst samples at 40 °C for 2 h. Thereafter the sample was flushed for 1 h with N_2 (30 cm³/min) to remove weaker held species so that only the chemisorbed H_2S species remained on the surface. H_2S -TPD was performed under 30 cm³/min N_2 flow with a temperature ramp from 40 to 750 °C (10 °C/min). Desorbed H_2S was measured with a mass spectrometer (ThermoStarTM, Pfeiffer Vacuum).

2.2. Catalyst characterization by probing with MeOH

The surface properties of the catalysts were probed with methanol. MeOH-DRIFTS experiments were performed to yield information about the surface based on the specific vibrations of the formed methoxy species. MeOH-TPSR was carried out on the

calcined and sulfided catalysts to study the chemical nature of the surface sites and the effect of H_2S .

2.2.1. *In situ* DRIFTS-MS measurements with MeOH surface probing

The surface species formed during methanol decomposition on the calcined ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ samples were studied by *in situ* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy combined with mass spectrometry (MS). The DRIFTS measurements were performed using a Nicolet Nexus FTIR spectrometer and a Spectra-Tech high temperature/high pressure reaction chamber with ZnSe windows. Gaseous products were monitored on-line by a mass spectrometer (Omnistar, Pfeiffer Vacuum). The spectrum of an aluminum mirror measured under nitrogen flow was used as the background, and the outlet was continuously analyzed by MS. The total gas flow rate was kept at 50 cm³/min.

Methanol decomposition was studied as a function of temperature from 100 to 500 °C. A fresh sample was used in each experiment and pre-treated by *in situ* calcination with 10% O_2/N_2 (AGA, air 99.999%, N_2 99.999%) at 600 °C for 2 h. The methanol feed (2000 ppm MeOH in N_2 , AGA) was started at 100 °C and continued at this temperature for 30 min. Spectra were collected once every minute (4 cm⁻¹ resolution, 30 scans) for the first 10 min, and thereafter once every 5 min (100 scans). After 30 min the sample cell was flushed with nitrogen to obtain a spectrum without the contribution by gas-phase methanol. Then methanol was redirected to the cell and the temperature was increased stepwise to 200 °C. Spectra were recorded every 25 °C (100 scans). At 200 °C, the sample cell was flushed with nitrogen and a spectrum was recorded. Thereafter, the methanol flow was resumed and the temperature increased. The experiment was continued by feeding methanol vapor to the chamber during heating with spectra collected every 25 °C (100 scans). Nitrogen flushes were done at 300, 400, and 500 °C. At 500 °C the sample was flushed with nitrogen and oxidized with diluted air.

2.2.2. Temperature-programmed surface reaction of MeOH

The temperature-programmed surface reaction of MeOH (MeOH-TPSR) of the ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ samples were carried out using 0.2 g of particles with a size distribution between 0.425 and 0.85 mm, made from crushed pellets. The ZrO_2 powders used to obtain those pellets had all been calcined at 800 °C. The ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$ samples were first calcined in O_2/He gas mixture (20 vol-% O_2 in He) from room temperature to 550 °C (ramp 10 °C/min) to remove adsorbed moisture and possible carbonaceous residues. The sample was transferred to a stainless steel reactor of 1 cm diameter, which was kept at 100 °C. Methanol adsorption for the calcined samples was performed under a total flow of 100 cm³/min, $P = 110$ kPa, of a 2000 ppm methanol in Ar. After complete saturation of the sample, the sample was purged with Ar at a flow rate of 50 cm³/min. Thereafter the temperature was increased to 700 °C (temperature ramp 10 °C/min) under Ar flow. The detection of the desorbing gases at the microreactor outlet was performed by mass spectrometry (Omnistar, Balzers), using a Channeltron detector.

To study the effect of H_2S on the catalysts, the samples were sulfided prior to MeOH-TPSR experiments. After calcination, the catalyst sample (0.2 g) was transferred to a Pyrex microreactor of 5 mm diameter, operating with a total flow of 50 cm³/min, $P = 110$ kPa. After a pre-treatment at 100 °C with H_2S (30 vol-% in H_2), the system was cooled to room temperature in a nitrogen atmosphere. Subsequently, the sample was transferred to stainless steel microreactor and MeOH-TPSR was carried out following the same procedure as for the calcined samples.

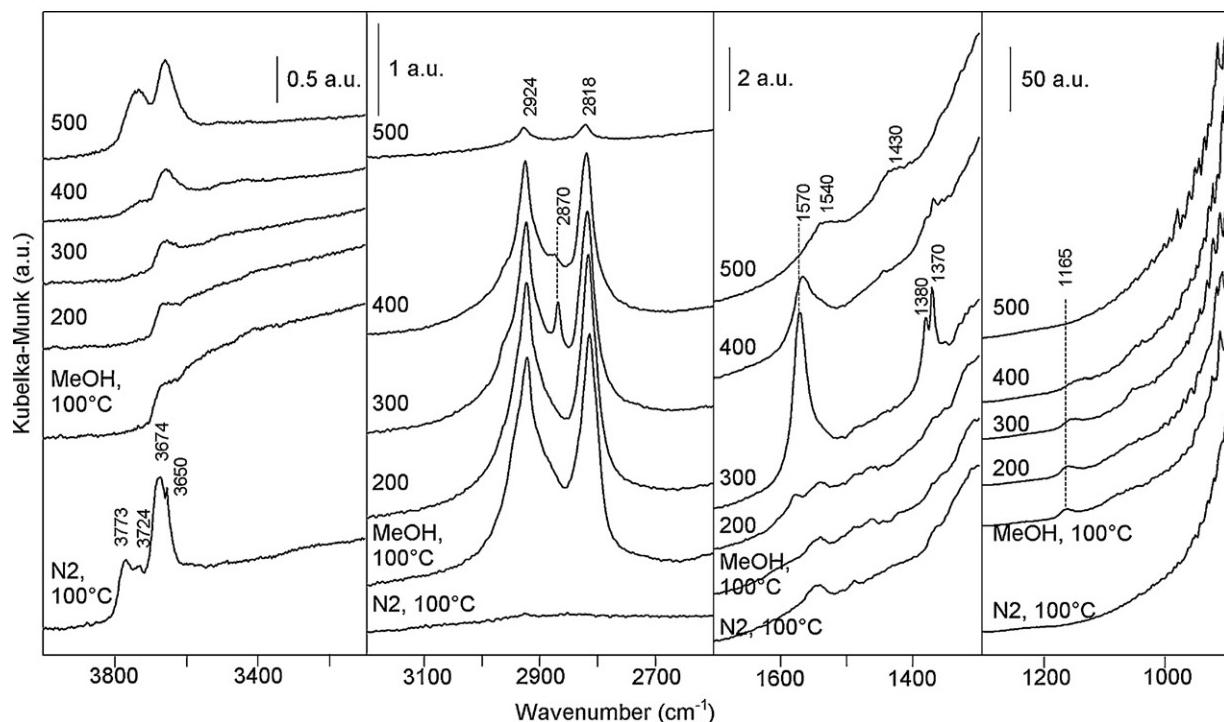


Fig. 1. In situ DRIFT spectra measured for pure ZrO_2 during temperature-programmed experiment with methanol.

3. Results and discussion

3.1. MeOH probe reaction on the calcined samples

3.1.1. MeOH DRIFTS results

Surface species formed during methanol adsorption and decomposition on the ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$ samples were

studied as a function of temperature with in situ DRIFTS; online MS analyzed the gaseous products formed.

Figs. 1–3 show selected spectra measured for the three catalysts during MeOH-DRIFTS experiments. The presented spectra were measured under nitrogen flow to minimize the effect of gas phase methanol. The peak positions were similar under methanol, which increased the intensities of the absorption bands.

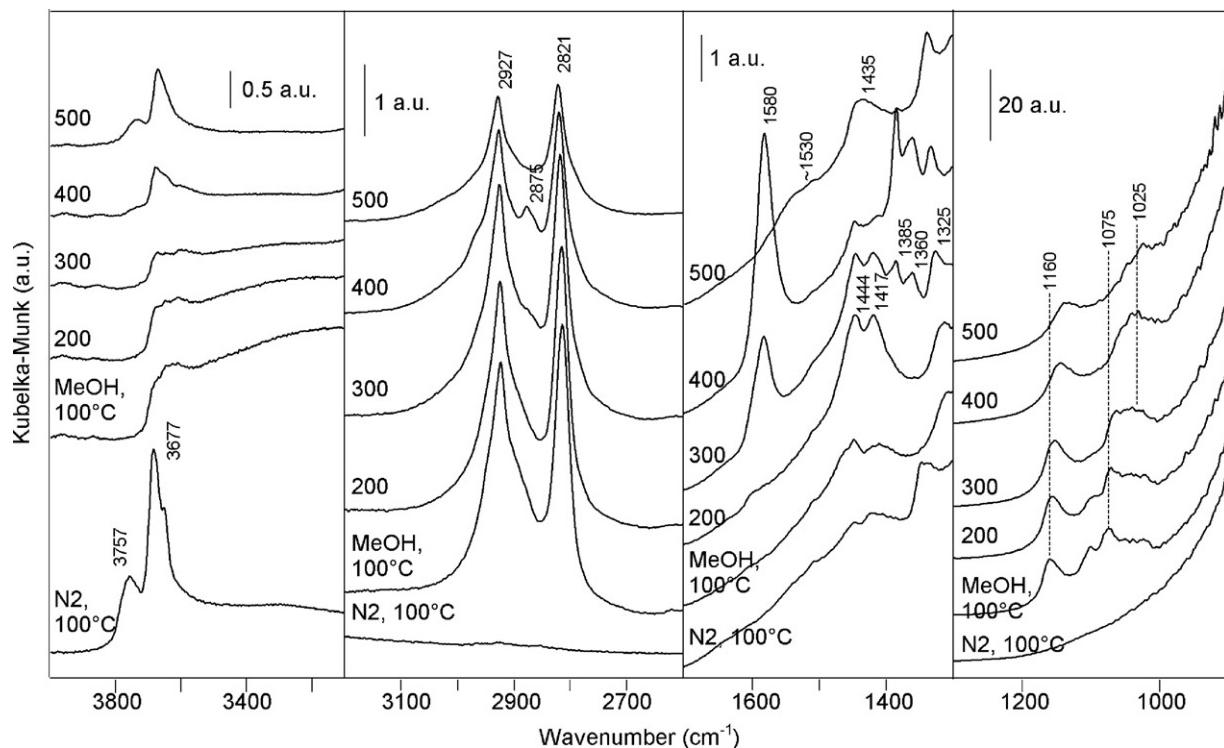


Fig. 2. In situ DRIFT spectra measured for $\text{Y}_2\text{O}_3\text{-ZrO}_2$ during temperature-programmed experiment with methanol.

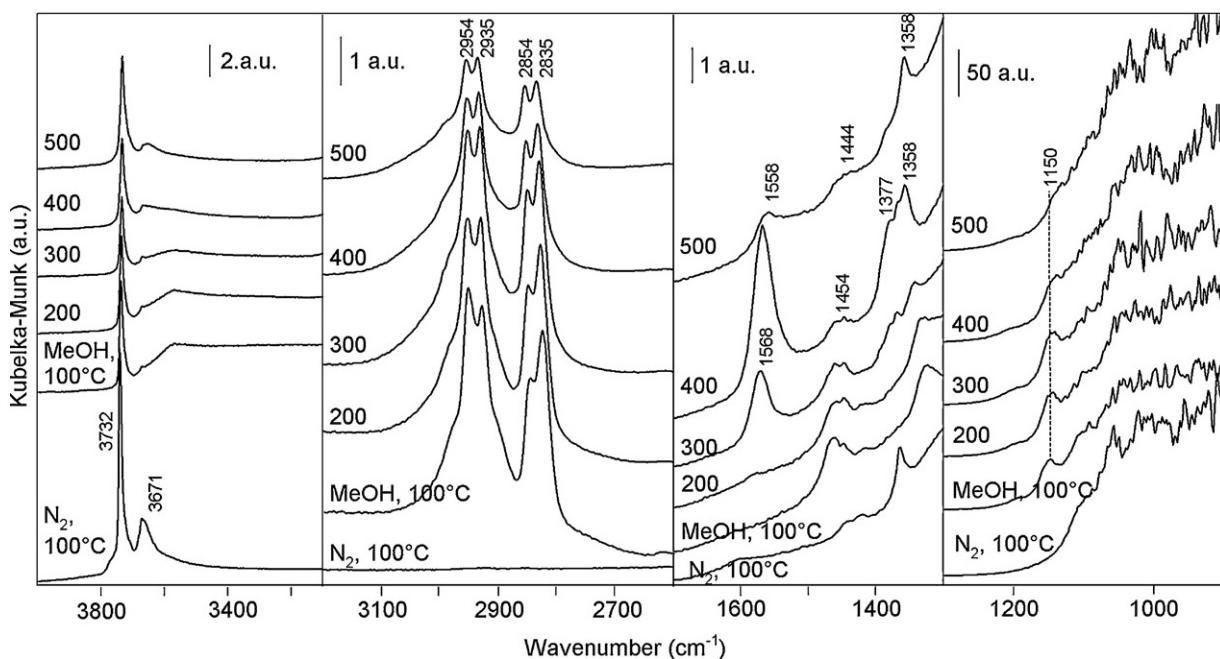


Fig. 3. In situ DRIFT spectra measured for $\text{SiO}_2\text{-ZrO}_2$ during temperature-programmed experiment with methanol.

The calcined ZrO_2 sample (Fig. 1) showed peaks due to hydroxyl groups at 3773, 3724, 3674 and 3650 cm^{-1} . The first three are assigned to terminal Zr-OH , bibridged $(\text{Zr})_2\text{-OH}$ and tribridged $(\text{Zr})_3\text{-OH}$ groups, respectively, on monoclinic zirconia [2,7]. Adsorption of methanol on the calcined zirconia at 100°C resulted in consumption of hydroxyl groups and appearance of hydrogen-bonded hydroxyls (broad band centered at ca. 3400 cm^{-1}). New peaks appeared at 2920 and 2815 cm^{-1} attributed to the $\nu_{\text{as}}(\text{CH}_3)$ and $\nu_s(\text{CH}_3)$ vibrations of methoxy species on zirconia (Zr-OCH_3), and at 1165 cm^{-1} due to $\nu(\text{OCH}_3)$ vibration of on-top methoxy species [13,20]. Molecularly adsorbed methanol may have been present, as suggested by a shoulder at 2950 cm^{-1} [13]. The methyl deformation band was seen at 1460 cm^{-1} [13].

Heating ZrO_2 above 250°C led to new peaks at 1573 , 1380 and 1370 cm^{-1} due to $\nu_{\text{as}}(\text{COO})$, $\delta(\text{CH})$, and $\nu_s(\text{COO})$ vibrations of formates [13]. The formate $\nu(\text{CH})$ peak at 2870 cm^{-1} was apparent from 275°C . The formates disappeared above 450°C whereas methoxy species were still apparent at 500°C . In addition, peaks of carboxylate or carbonate [13] species were present at approximately 1540 and $\sim 1430\text{ cm}^{-1}$ at 500°C , and a gradual reappearance of hydroxyl groups with temperature was observed during the entire experiment.

The calcined $\text{Y}_2\text{O}_3\text{-ZrO}_2$ sample (Fig. 2) exhibited peaks at 3757 and 3677 cm^{-1} , which are, in accordance with earlier results obtained for this sample [2], attributed to terminal and tribridged hydroxyl groups, respectively, on tetragonal Y_2O_3 -doped zirconia [21]. Adsorption of methanol resulted in consumption of hydroxyl groups and in appearance of methoxy peaks at 2920 , 2810 , and 1160 cm^{-1} similar to the calcined ZrO_2 sample. Additional peaks were seen at 1444 , 1417 , 1075 , and 1025 cm^{-1} during heating at 200°C and above. Formates at 2877 , 1580 , 1382 and 1356 cm^{-1} became increasingly apparent at 300 and above, along with carboxylates/carbonates (1446 and 1335 cm^{-1}). Hydroxyl groups were partly restored with temperature.

The calcined $\text{SiO}_2\text{-ZrO}_2$ sample (Fig. 3) showed peaks at 3732 and 3671 cm^{-1} due to silanol Si-OH species, and tribridging hydroxyl groups on zirconia, respectively [2]. With adsorption of methanol the intensities of these hydroxyl groups decreased, whereas a new hydroxyl band appeared at 3572 cm^{-1} possibly

due to molecularly adsorbed methanol and/or hydrogen-bonded hydroxyls. Two types of methoxy species were seen: Zr-OCH_3 at 2927 , 2830 , 1443 , and 1150 cm^{-1} , and Si-OCH_3 at 2953 , 2850 , and 1461 cm^{-1} [19]. With increasing temperature, formates appeared above 250°C , but the peak intensities were lower than for the other samples. Furthermore, no formate $\nu(\text{CH})$ peak was observed at approximately 2880 – 2870 cm^{-1} . This may indicate that the formation of the formate species was not as significant on this sample as on the other ones. The methoxy groups were present still at 500°C , and carbonate/carboxylate-type species were also seen (1560 , 1455 , and 1352 cm^{-1}).

Simultaneous mass spectrometry results (not shown) indicated formation of H_2 with all three samples above 250°C with the amount continuously increasing with temperature. DME formation was seen only on the $\text{SiO}_2\text{-ZrO}_2$ sample between 300 and 400°C . A small amount of CO_2 was produced with the calcined ZrO_2 and the $\text{SiO}_2\text{-ZrO}_2$ samples at above 400°C . In addition, methyl fragments were detected throughout the whole temperature range. Other products that may form from methanol include formaldehyde and carbon monoxide but their formation could not be detected due to overlapping of their mass numbers with other components.

3.1.2. Temperature-programmed surface reaction of MeOH on the calcined samples

The MeOH-TPSR experiments on the ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ were carried out to determine the effect of H_2S on the catalyst properties. For this the changes in the MeOH-TPSR product distribution were compared for the calcined and sulfided samples. The formation of DME is presented in Fig. 4 for the calcined and sulfided samples. For CO_2 , formaldehyde, CO , and H_2 the T_{max} values and the corresponding peak areas are presented in Tables 1 and 2, respectively. The changes due to pre-adsorbed H_2S are discussed in the next section.

Fig. 4 shows that the amount of DME generated decreased in the order $\text{SiO}_2\text{-ZrO}_2 > \text{Y}_2\text{O}_3\text{-ZrO}_2 \gg \text{ZrO}_2$. Desorption temperature is lower for ZrO_2 (350°C) than for $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ (480 and 370°C , respectively).

CO_2 is produced on a wide temperature range on all the catalysts (T_{max} of the most intense peak shown in Table 1). Two CO_2

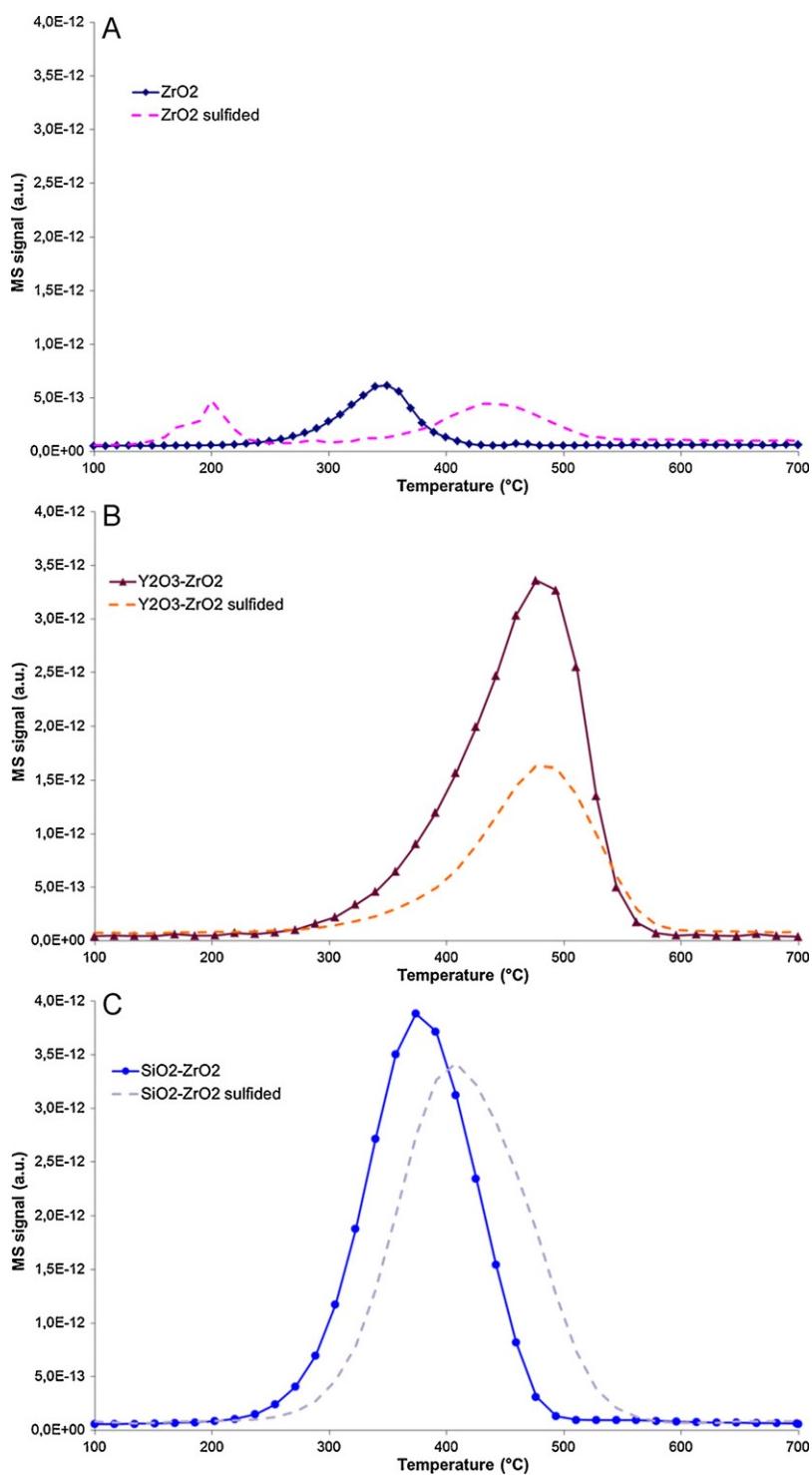


Fig. 4. DME MS-signal ($m/z=45$) in the MeOH-TPD experiment on calcined and sulfided ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$.

Table 1

T_{\max} (°C) for formaldehyde, CO_2 , CO and H_2 during MeOH-TPSR experiment on calcined and sulfided ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$ (the most intense maximum is reported, shoulders in the parentheses).

Sample	Formaldehyde	CO_2	CO	H_2
ZrO_2	170	580 (170, 380)	400 (300)	400
ZrO_2 (sulf.)	200	580 (150, 420)	510 (400)	510
$\text{Y}_2\text{O}_3\text{-ZrO}_2$	220	350	580	580
$\text{Y}_2\text{O}_3\text{-ZrO}_2$ (sulf.)	220	290	560 (420)	560
$\text{SiO}_2\text{-ZrO}_2$	250	560 (360)	510 (370)	510 (370)
$\text{SiO}_2\text{-ZrO}_2$ (sulf.)	220	530 (270)	550	550

Table 2

Peak areas ($\text{a.u. s} \times 10^{-8}$) for formaldehyde, CO_2 , CO and H_2 during MeOH-TPSR experiment on calcined and sulfided ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$.

Sample	Formaldehyde	CO_2	CO	H_2
ZrO_2	0.077	0.047	2.46	1.13
ZrO_2 (sulf.)	0.109	0.052	5.51	0.826
$\text{Y}_2\text{O}_3\text{-ZrO}_2$	0.474	0.115	4.49	3.46
$\text{Y}_2\text{O}_3\text{-ZrO}_2$ (sulf.)	0.236	0.070	4.12	1.69
$\text{SiO}_2\text{-ZrO}_2$	0.338	0.155	4.29	3.54
$\text{SiO}_2\text{-ZrO}_2$ (sulf.)	0.306	0.019	4.41	3.30

maxima are detected on the $\text{SiO}_2\text{-ZrO}_2$ catalyst, whereas $\text{Y}_2\text{O}_3\text{-ZrO}_2$ shows only a broad maximum. ZrO_2 shows only minor formation of CO_2 with multiple maxima. CO_2 production on the studied catalysts decreased in the $\text{SiO}_2\text{-ZrO}_2 \gg \text{Y}_2\text{O}_3\text{-ZrO}_2 > \text{ZrO}_2$ order (Table 2).

Table 2 shows that the amount of formaldehyde formed on the catalysts decreases in the order $\text{Y}_2\text{O}_3\text{-ZrO}_2 > \text{SiO}_2\text{-ZrO}_2 > \text{ZrO}_2$. Formaldehyde desorbs on a wide temperature range. The peak maxima appear, however, at low temperatures (Table 1). Also MeOH desorbs at approximately this temperature (not shown), which is attributed to desorption of molecular MeOH present on the catalysts or the reverse reaction of the methoxy species [13].

In Table 1, the CO and H_2 T_{\max} values for the calcined $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ are higher (~580 and 510 °C, respectively) than those on the calcined ZrO_2 sample (~400 °C). The CO peaks for ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$ appear concurrently with the H_2 peaks (Table 1). The peaks on the $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$ are more intense than on the ZrO_2 (Table 2).

3.1.2.1. Methanol adsorption and reaction pathways. Methanol may adsorb on oxide surfaces either molecularly or dissociatively. The dissociative adsorption has been suggested to take place via two ways: by adsorption on surface hydroxyl groups with formation of methoxy groups and water, or on c.u.s. $\text{Zr}^{4+}\text{-O}^{2-}$ pairs with formation of methoxy- and hydroxyl groups [18,19]. As noted during the MeOH-DRIFTS experiments, hydroxyl groups decreased in intensity during the adsorption of methanol on all three samples, suggesting that dissociative adsorption took place on the hydroxyl groups, which would be substituted by the methoxies.

MeOH-DRIFTS results show the formation of only one type of methoxy species with the calcined ZrO_2 and $\text{Y}_2\text{O}_3\text{-ZrO}_2$ samples, and two types of species with the $\text{SiO}_2\text{-ZrO}_2$ sample. This suggests that yttria is homogeneously distributed in the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ sample and it does not form a separate phase; whereas the silica and the zirconia phases are more separate and two distinct methoxy groups can be formed on the $\text{SiO}_2\text{-ZrO}_2$ sample.

Methoxy groups react on catalyst surface to produce DME via condensation of two methoxy groups [18]. DME selectivity is used to describe the pure dehydration ability of the catalyst, related generally to its Lewis acidic character [14,16]. Based on the intensities of the DME peaks during MeOH-TPSR (Fig. 4), it is concluded that catalyst acidity for the calcined samples decreases in the order $\text{SiO}_2\text{-ZrO}_2 > \text{Y}_2\text{O}_3\text{-ZrO}_2 \gg \text{ZrO}_2$ in agreement with previous studies on these catalysts [2]. This is in accordance with the MeOH-DRIFTS results, which also indicated highest number of Lewis acidic sites on the $\text{SiO}_2\text{-ZrO}_2$ sample, and also with Bosman et al. [22] who reported that doping ZrO_2 with SiO_2 increases the acidity [22]. The Lewis acid sites were comparatively weak on the ZrO_2 sample as indicated by the relatively low temperature of desorption for DME (Fig. 4), also in agreement with previous studies on the same catalysts [2].

During the MeOH-DRIFTS experiments the peaks of the methoxy species decreased in intensity with increasing temperature on all three samples, whereas those of the formate species became apparent near 300 °C, and thereafter decreased before 500 °C. This suggests that the methoxy species formed in the dissociative adsorption of methanol reacted to formate (HCOO^*) species. Similar trends have already been reported for methanol decomposition on zirconia-based catalysts [18]. The transformation of methoxy to formate has been suggested [23] to proceed through an intermediate dioxyethylene species, an adsorbed form of formaldehyde. Dioxyethylene may decompose to gas-phase formaldehyde on the redox sites [14].

Wang and Wachs associate formaldehyde formation with redox sites on the catalyst [14]. However, some studies also suggest that the formation of formaldehyde may be connected with basic O^{2-} sites and the reducibility of the catalyst [24,25]. Roozeboom

et al. concluded that the selectivity to formaldehyde increases with decreasing reducibility of the catalyst [25]. Formaldehyde may also be formed via a reaction between methanol and hydroxyl group [19]. Based on the generation of formaldehyde (Tables 1 and 2) the redox sites on ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$, and $\text{SiO}_2\text{-ZrO}_2$ catalysts are suggested to be varied, since formaldehyde production differed. A small part of the formaldehyde could come from reactions of methanol and hydroxyl groups, since methanol desorbed at the same time. Also, according to Viinikainen et al. the redox properties of these oxides differ, which affects their reactivity towards oxidation reactions during gasification gas clean-up [2].

CO_2 may be originated from the decomposition of formate and/or carbonate species [18,26], which were present on all the catalysts during MeOH-DRIFTS experiments above 300 °C and after (however, formates mostly disappeared before 500 °C, whereas carbonates/carboxylates were still present). The formation of CO_2 acts as an indicator of the MeOH oxidation processes [16]. In general it can be used to depict the Lewis basicity of the catalyst [14,16,18,27,28]. This was demonstrated by Garcia Cortez et al. who performed MeOH-TPSR experiments on $\text{VO}_x/\text{Al}_2\text{O}_3$ with different amounts of K doping, clearly showing the increase in CO_2 production with increasing basicity of the catalyst [27]. In the MeOH-DRIFTS experiments (MS results, not shown) CO_2 forms on ZrO_2 and $\text{SiO}_2\text{-ZrO}_2$ samples, suggesting that these had more basic sites than the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ sample. However, during MeOH-TPSR experiments CO_2 formation decreased in the order $\text{SiO}_2\text{-ZrO}_2 \gg \text{Y}_2\text{O}_3\text{-ZrO}_2 > \text{ZrO}_2$, illustrating the order of the Lewis basicity of the catalysts (Table 2).

In the MeOH-DRIFTS experiments the methoxy species detected on $\text{SiO}_2\text{-ZrO}_2$ were Zr-OCH_3 and Si-OCH_3 . Apparently separate formates appeared with increasing temperature (above 250 °C). It is thus probable that the methoxy species on the $\text{SiO}_2\text{-ZrO}_2$ sample evolve to formates yielding the two CO_2 peaks reported in Table 1 (at ~360 and 560 °C, the latter being very intense). Also, only one DME peak is observed in the MeOH-TPSR experiments for $\text{SiO}_2\text{-ZrO}_2$. The formation of CO_2 was low on the ZrO_2 catalyst (Table 2) suggesting that the strength of its basic sites is rather weak. This is consistent with Korhonen who reported that highly basic c.u.s. sites were not observed on ZrO_2 [26]. Also Bianchi et al. observed the generation of CO_2 to be minor in a MeOH-TPSR experiment on ZrO_2 aerogel [18]. The higher formation of CO_2 with $\text{Y}_2\text{O}_3\text{-ZrO}_2$ compared to ZrO_2 was expected since its surface was reported to consist mainly of strongly basic O^{2-} centers [2].

The simultaneous production of CO and H_2 means that they must originate from the decomposition of formate or methoxy species [18,19]. The CO and H_2 T_{\max} on ZrO_2 at lower temperatures (Table 1) suggest that the formate groups on the ZrO_2 were more reactive than the ones on $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$. According to Badlani and Wachs the surface methoxy decomposition temperature for ZrO_2 is 326 °C and 560 °C for SiO_2 [17].

MeOH probing showed differences in the catalyst characteristics. $\text{SiO}_2\text{-ZrO}_2$ possessed stronger Lewis acidic and basic properties compared to the pure ZrO_2 and $\text{Y}_2\text{O}_3\text{-ZrO}_2$. The redox properties of $\text{Y}_2\text{O}_3\text{-ZrO}_2$ are stronger than on the other catalysts studied. It was also suggested, that doping ZrO_2 with yttria or silica results in different kind of distribution of the dopants in ZrO_2 phase; silica exists as separate phases on $\text{SiO}_2\text{-ZrO}_2$, whereas the distribution of yttria in $\text{Y}_2\text{O}_3\text{-ZrO}_2$ is more homogeneous.

3.2. H_2S retention on the surfaces and the effect of H_2S on the properties of ZrO_2 -based catalysts

H_2S adsorption on metal oxides has been suggested to proceed via the following pathways: (1) exchange of surface oxygen to sulfur whereupon water is desorbed, (2) dissociative adsorption of H_2S to HS^- and H^+ with formation of a surface hydroxyl group [5], or a

water molecule if the dissociation of H₂S occurs on an OH⁻ group [6], and (3) coordinatively bonded hydrogen sulfide [29].

Pathway 1 can also be described as an interaction of H₂S with a defective site, or oxygen vacancy, which involves incorporation of S²⁻ in the lattice [30].

3.2.1. Temperature-programmed desorption of H₂S

H₂S adsorption and desorption was studied for the ZrO₂, Y₂O₃-ZrO₂ and SiO₂-ZrO₂ samples to investigate the interaction of H₂S with the catalyst surface. Pure SiO₂ was also tested; however, virtually no sulfur compounds were detected in the H₂S-TPD spectrum (results for the pure SiO₂ sample not shown), showing the inert nature of SiO₂. Also Travert et al. [6] found that on SiO₂, only undissociative adsorption of H₂S occurs. Thus, it seems that undissociatively adsorbed H₂S is relatively easily desorbed, as also indicated earlier by Datta and Cavell [31].

Water was produced during H₂S adsorption on all the samples (not shown). This indicates the dissociative adsorption of H₂S via exchange of surface oxygen to sulfur, or via the replacement of the surface hydroxyl groups by SH⁻ groups, both pathways resulting in water generation [5,6,30]. H₂S was found to dissociate on ZrO₂ surfaces at higher temperatures (room temperature and above) also by Travert et al. [6]. Fig. 5 shows the H₂S desorption profiles. The high temperature region is not shown, since no H₂S desorbed after ~300 °C. A minor peak for SO₂ was detected only on SiO₂-ZrO₂ at 660 °C (not shown), suggesting that the sulfur may also react with lattice oxygen.

The H₂S-TPD profiles (Fig. 5) showed one maximum for ZrO₂ at 100 °C and for Y₂O₃-ZrO₂ at 115 °C. The SiO₂-ZrO₂ sample had two distinct maxima; one at 115 °C and another one at 210 °C, the latter being very intense indicating strong H₂S adsorption. This suggests that H₂S occupies different sites on SiO₂-ZrO₂ than it does on ZrO₂ and Y₂O₃-ZrO₂. Sulfur retention on the surface after TPD cannot be ruled out.

The surface characterization in the earlier studies [2] and MeOH probing of the three ZrO₂-based catalysts indicated that the surface sites of these catalysts were different. It has also been established, that oxygen mobility is enhanced on the Y₂O₃-ZrO₂ catalyst compared to the pure ZrO₂ [11], whereas on the SiO₂-ZrO₂ oxygen mobility is more limited due to the strong covalent nature of the Si-O bond [12]. The intensity order of the H₂S peak at approximately 100 °C is Y₂O₃-ZrO₂ > ZrO₂ > SiO₂-ZrO₂, which corresponds to the order in which oxygen vacancies are generated [2,12], and also to the order in which H₂S affects the reactivity in the gasification gas application. It is suggested that this peak be due to dissociative adsorption of H₂S and H₂S adsorption via replacement of oxygen in the lattice.

IR results indicated two phases on SiO₂-ZrO₂, which could explain the two H₂S desorption peaks detected in its H₂S desorption spectrum. However, pure SiO₂ did not adsorb hydrogen sulfide. Therefore it is not expected that H₂S adsorbs on the SiO₂ phase on SiO₂-ZrO₂ but may however be adsorbed on an "interphase". According to characterization studies, highly acidic Zr⁴⁺ centers were only present on SiO₂-ZrO₂ [2]. Thus, the H₂S desorption peak at 210 °C observed on SiO₂-ZrO₂ may be connected to the dissociative adsorption of H₂S on the Zr⁴⁺ acid sites, or the adsorption of H₂S on some SiO₂-ZrO₂ interphase.

3.2.2. Temperature-programmed surface reaction of MeOH on the sulfided samples

MeOH-TPSR experiments on the sulfided ZrO₂, Y₂O₃-ZrO₂ and SiO₂-ZrO₂ samples were performed to study the effect of H₂S on catalysts characteristics.

During the adsorption of MeOH on the sulfided catalyst surface at 100 °C, no sulfur-containing species were detected in the mass spectra (adsorption profiles not shown). No H₂S was also detected

during MeOH-TPSR. Thus, H₂S cannot be replaced by MeOH during its adsorption, indicating strong adsorption of H₂S. More water desorbed during adsorption of MeOH from the sulfided samples than from the calcined ones, which may suggest increased number of surface hydroxyl groups after sulfidation.

Fig. 4 shows that the amount of DME produced on the sulfided Y₂O₃-ZrO₂ sample was lower than on the calcined Y₂O₃-ZrO₂-sample, whereas a similar decrease was not as evident on the ZrO₂ or SiO₂-ZrO₂ samples. With ZrO₂ and SiO₂-ZrO₂ however, the temperature of the DME peak shifted upwards. This suggests that sulfur adsorption affected the nature of the Lewis acid sites on ZrO₂ and SiO₂-ZrO₂ (the adsorption of DME stronger on the sulfided ZrO₂ and SiO₂-ZrO₂ sample). It is suggested that at least part of the H₂S adsorbed on the Lewis acidic sites responsible for DME production on all the catalysts studied or that the adsorption of H₂S changed the nature of these sites. Also Travert et al. [6] found that on a ZrO₂ catalyst, sulfur adsorbs partly on its Lewis acidic sites [6].

Sulfidation increased CO₂ production for the ZrO₂ catalyst (Table 2). On the contrary, for the SiO₂-ZrO₂ catalyst, sulfidation significantly decreased CO₂ production (Table 2). On Y₂O₃-ZrO₂ the change was not as evident, however a slight decrease in the intensity of CO₂ peak and temperature of desorption was seen. It is suggested that H₂S treatment enhanced the basic properties of the ZrO₂ catalyst (or, moreover, the mobility of surface oxygen) responsible for CO₂ production, whereas on the SiO₂-ZrO₂ catalyst the basic character was markedly reduced. This is in accordance with the earlier suggestion by Rönkkönen et al. that sulfur influences the basic properties of these catalysts [4].

3.2.2.1. DMS formation. Dimethyl sulfide (DMS) was identified during MeOH-TPSR as shown in Fig. 6, indicating that the pre-adsorbed H₂S reacted with MeOH to DMS. The T_{max} for DMS on the studied samples is at approximately 490–530 °C. A shoulder is seen on SiO₂-ZrO₂ at 390 °C. No H₂S or other sulfur-containing molecules were detected during MeOH adsorption (not shown), indicating that the species from pre-adsorbed H₂S were not replaced by the adsorbing MeOH. This and the high DMS T_{max} values indicate that sulfur is rather strong bound to the surface.

The amount of DMS formed decreased in the order Y₂O₃-ZrO₂ > ZrO₂ > SiO₂-ZrO₂, which is the same order as that of H₂S desorbed at around 100 °C in the H₂S-TPD experiments (Fig. 5). Y₂O₃-ZrO₂ had the highest amount of adsorbed sulfur species or the adsorbed sulfur species were more reactive, as indicated by the amount of DMS formed. When comparing the results of SiO₂-ZrO₂ in the H₂S-TPD and MeOH-TPSR experiments, two maxima are detected for H₂S and DMS (Figs. 5 and 6) indicating at least two sites for H₂S adsorption and DMS generation on SiO₂-ZrO₂. The temperature difference between the H₂S T_{max} and DMS T_{max} does not allow one to conclude that the same sulfur species are present in the H₂S-TPD and MeOH-TPSR experiments. Nevertheless, the different behavior of SiO₂-ZrO₂ in both experiments is noted.

Very few studies on MeOH adsorption on sulfided catalysts have been reported, yet the reaction between MeOH and H₂S on metal oxides catalysts and DMS formation was reported by Ziolek et al. [32]. DMS formation pathways on ZrO₂ catalysts are still unknown, since the active form of sulfur from adsorbed H₂S has not been established. However, literature suggests, that the reaction to DMS occurs between SH⁻ and/or S²⁻ (formed in the dissociative adsorption of H₂S [5,6]) and methoxy species [32].

According to Travert et al. [6] a H₂S-treated ZrO₂ surface has a higher amount of hydroxyl groups, which are believed to have increased Brønsted acidic character. On the contrary, they reported that SH groups did not reveal any proton-donating ability [6]. The sulfided surface may also have increased redox or basic properties because of the adsorbed sulfur replaced an oxygen atom in the lattice, as suggested by Ziolek et al. [5]. This was related with the

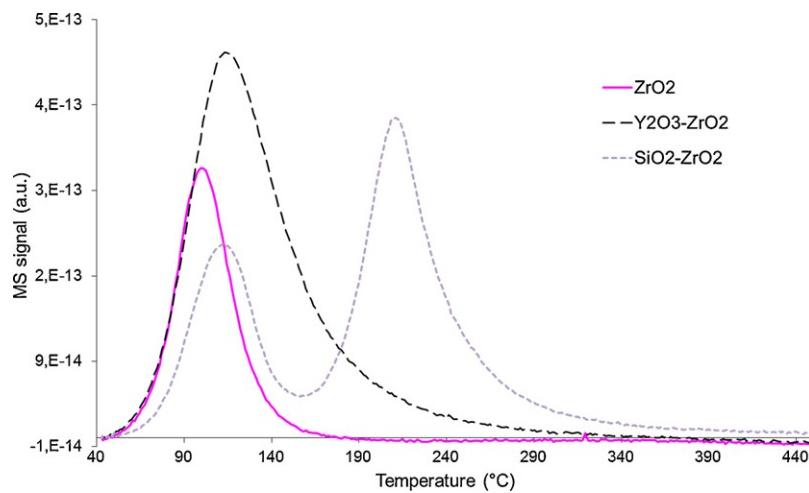


Fig. 5. H₂S-TPD-profiles of the studied ZrO₂, Y₂O₃-ZrO₂ and SiO₂-ZrO₂ catalysts ($m/z=34$).

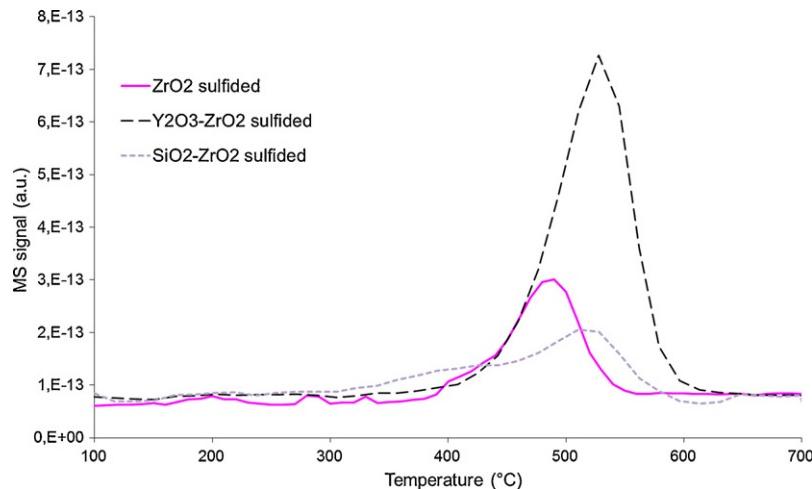


Fig. 6. MS-signal ($m/z=47$) illustrating the generation of DMS in the MeOH-TPD experiment on ZrO₂, Y₂O₃-ZrO₂, and SiO₂-ZrO₂.

lower electronegativity of S²⁻ compared to O²⁻ [5]. In view of this, Fig. 7 presents the sulfided ZrO₂ surface with the “new” hydroxyl groups acting as acid and the adjacent sulfur atom as a base, following DMS formation as speculated. It is possible that upon the adsorption of MeOH on the sulfided surface water is released from MeOH during its adsorption (Fig. 7) and DMS is generated via the reaction of CH₃S and methoxy groups (Fig. 7). It is thus speculated that sulfur on the surfaces of the studied ZrO₂ catalysts acted as a base and caused MeOH to react by donating its OH⁻ group (breaking of C–O bond in MeOH). This may explain the greater amounts of desorbing water during MeOH adsorption on the sulfided ZrO₂ surfaces compared to those amounts on the calcined ZrO₂ surfaces in our experiments. It may be the combination of the two features (increased number of Brønsted acidic OH⁻ groups and the more basic sulfur atoms compared with O²⁻) that acts as a source for the observed reactivity towards the conversion of methanol to DMS.

It is also possible, that the reaction occurs between the methoxy and SH⁻ species. However, during the MeOH-TPSR experiments it was noted that sulfur is very strongly bound to the surface, and the elimination of SH⁻ groups would have been expected during MeOH adsorption. Moreover, the amount of the generated DMS on different catalysts decreases in correlation with the order in which oxygen vacancies are generated (Y₂O₃-ZrO₂ > ZrO₂ > SiO₂-ZrO₂), which suggests the active form of sulfur in the lattice. The migration of S in to the lattice during TPSR can neither be ruled out. In summary, DMS formation possibly involves interaction with a sulfur atom incorporated in the lattice of the ZrO₂ catalysts. DMS is formed most probably via the condensation of CH₃S and CH₃O species.

Based on our study, there is a clear difference in the behavior of the studied ZrO₂-based catalysts with H₂S, SiO₂-ZrO₂ possessing the most diverging characteristics. The adsorbed H₂S has different reactivities on the surfaces of the ZrO₂-based catalysts, as indicated

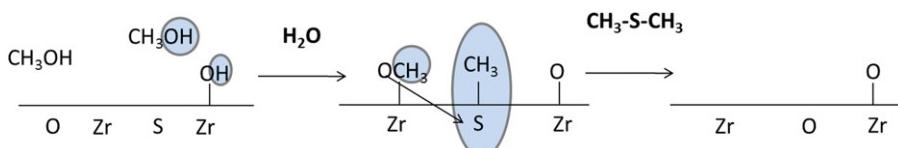


Fig. 7. Suggested pathway for MeOH adsorption and the generation of DMS on the sulfided ZrO₂ catalysts.

by the DMS profiles, which can be correlated to the observed effect in naphthalene conversion during gasification gas clean-up. Based on the results from MeOH-TPSR on sulfided catalysts, it is speculated that the limited reactivity of H₂S on SiO₂-ZrO₂ hinders its activity during gas cleaning (whether some sulfur is irreversibly adsorbed cannot be concluded here but is subject to further study). It is also suggested, that the interaction of sulfur with the lattice is seen in the gasification gas clean-up as an enhancement effect on Y₂O₃-ZrO₂ and ZrO₂.

4. Conclusions

We probed surfaces of ZrO₂, Y₂O₃-ZrO₂, and SiO₂-ZrO₂ catalysts with the aim of explaining the differences between the samples regarding the H₂S-induced changes in naphthalene conversion during gasification gas clean-up; namely improvement on ZrO₂ and Y₂O₃-ZrO₂ compared to no effect or poisoning on SiO₂-ZrO₂. MeOH was used as a surface probe in addition to H₂S. The following conclusions can be drawn:

- (1) MeOH-DRIFTS experiments uncover the existence of two phases on SiO₂-ZrO₂, whereas yttria is more homogeneously distributed on/in Y₂O₃-ZrO₂. This probably explains the desorption profiles of H₂S, which differ for SiO₂-ZrO₂ compared to ZrO₂ and Y₂O₃-ZrO₂ (two peaks for SiO₂-ZrO₂ and one for the other catalysts). It is concluded that H₂S adsorption on ZrO₂ and Y₂O₃-ZrO₂ occurs mainly on one kind of sites and there are at least two H₂S adsorption sites on the SiO₂-ZrO₂. H₂S was found to adsorb dissociatively on ZrO₂ surfaces.
- (2) MeOH-TPSR products on sulfided ZrO₂ catalysts differed from those on the calcined samples showing that H₂S affected the reactivity of the surfaces. H₂S-treatment was also found to affect the nature of the acidic and basic sites on the ZrO₂ catalysts; Lewis acidity decreased especially on Y₂O₃-ZrO₂, whereas Lewis basicity was differently affected; on the ZrO₂ catalyst it increased and on the SiO₂-ZrO₂ it markedly decreased. The effect on the Lewis basicity of Y₂O₃-ZrO₂ was not as evident as on the other catalysts.
- (3) Sulfur reacted with methoxy species to DMS during heating. The amount of DMS formed was in the order Y₂O₃-ZrO₂ > ZrO₂ > SiO₂-ZrO₂, showing that the sulfur species were least reactive on SiO₂-ZrO₂. Two DMS desorption maxima were found on SiO₂-ZrO₂, whereas on the ZrO₂ and Y₂O₃-ZrO₂ DMS showed only one intense maximum.
- (4) The order of the generated DMS corresponds to the intensity of the sulfur effect on the properties of the catalysts in gasification gas clean-up, as well as the order of desorbed H₂S at around 100 °C in the H₂S-TPD experiments. This is also the order in which oxygen vacancies are expected to be generated on these catalysts.
- (5) H₂S adsorption on the sites present on ZrO₂ and Y₂O₃-ZrO₂ has a positive effect on naphthalene conversion during gasification gas clean-up which may be connected with the reactions of adsorbed sulfur on their surface. On the contrary, on SiO₂-ZrO₂ the observed poisoning effect may be due to reduced

reactivity of sulfur on the surface, which was illustrated by the lower amount of the sulfur-containing product from MeOH.

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